Structural and mechanical properties of phospholipid membranes hybridized with synthetic polymer rafts

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There is a long-term interest in creating artificial biomimetic membranes where self-assembled phospholipid bilayers are selectively permeabilized by synthetic channel-like molecules. One example is the co-assembly of amphiphilic block-copolymers with phospholipids into a hybrid membrane. Hybrid phospholipid block-copolymer bilayers display many properties seen in biomembranes such as selective transport phenomena, synergistic elastic properties, and structural phase transformations. Just like in biomembranes, these fundamental properties of hybrid bilayers are often regulated by lateral phase separation. Understanding the molecular and physical cues that determine the formation of rafts or domains in hybrid membranes, their size, and morphology is paramount to elucidating and programming their function. Employing a combination of coarse-grained molecular dynamics simulations and high-resolution cryogenic electron microscopy, we discovered that phosphatidylcholine-cholesterol bilayers hybridized with poly(butadiene-*b*-ethylene oxide) develop two distinct phase-separated morphologies. At molar fractions of polymer above 10 mol % the expected molecular distribution into lipid-rich and polymer-rich domains is observed. However, at low polymer content, a new structure develops in which the bilayer leaflets unzip (but remain continuous) to incorporate nanodomains of hydrophobic butadiene globules. We conjecture that unzipping is energetically more favorable than sustaining the hydrophobic mismatch between butadiene blocks and phospholipid acyl chains. These findings offer new insights into the morphology of biomembranes upon insertion of transmembrane proteins with bulky hydrophobic residues.

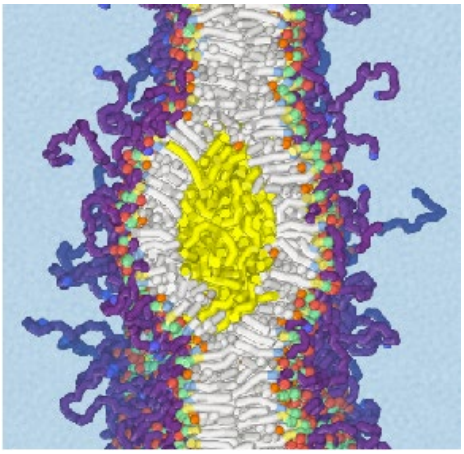

Figure 1: Polymer-lipid hybrid membrane.

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